

CLAIMS

1. A process for the preparation of a latex with predefined properties by emulsion (co)polymerization of at least one kind of
- 5 ethylenically unsaturated monomer, characterized in that the process is carried out with continuous *in situ* monitoring of the (co)polymerization comprising the following stages:
- (i) incident light radiation within the spectral
- 10 band situated between 200 nm and 1 400 nm, and preferably between 700 nm and 1 400 nm, is emitted into the emulsion,
- (ii) the light scattered by the reaction medium is picked up and transmitted to a Raman spectrometer,
- 15 (iii) the Raman spectrum, which shows the energy of the scattered light as a function of the difference in wavelength with respect to the incident light radiation, is determined,
- (iv)
- 20 a) either the intensities (areas or heights) of specific lines of the spectrum:
- of un(co)polymerized free monomer(s) in the reaction medium,
  - and of the polymer obtained,
- 25 b) or the concentrations of un(co)polymerized free monomer(s) in the reaction medium and of the polymer obtained are calculated from the Raman

spectrum using quantitative spectral analytical methods, these methods preferably being multivariable chemometric methods;

- (v) the process data are calculated either from the concentrations of free monomer(s) and of the polymer obtained or from the intensities (areas or heights) of specific lines of the spectrum of free monomer(s) in the reaction medium and from the intensities (areas or heights) of specific lines of the spectrum of the polymer obtained;
- (vi) these process data are compared with reference data specific to the process for the production of the latex with the predefined properties;
- (vii) and the reaction parameters, such as the temperature, the pressure, the stirring of the medium and the feeding with monomers, are adjusted in order to minimize the difference between the process data measured in-line and the reference process data.

2. The process as claimed in claim 1, characterized in that the Raman spectrometer is a Fourier transform or optical dispersive Raman spectrometer, preferably a Fourier transform Raman (FT-Raman) spectrometer.

3. The process as claimed in the preceding claim, characterized in that the latex results from the emulsion (co)polymerization of ethylenically unsaturated monomers chosen from the group consisting:

- of styrene and/or its derivatives, in particular derivatives such as  $\alpha$ -methylstyrene or vinyltoluene;
- of dienes, such as butadiene, isoprene or 2-chloro-1,3-butadiene;
- of (meth)acrylic esters, this term denoting esters of acrylic acid and of methacrylic acid with hydrogenated or fluorinated  $C_1$ - $C_{12}$ , preferably  $C_1$ - $C_8$ , alcohols, in particular methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, tert-butyl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate or isobutyl methacrylate;
- of vinyl nitriles, preferably those having from 3 to 12 carbon atoms, such as acrylonitrile and methacrylonitrile;
- of carboxylic acid vinyl esters, such as vinyl acetate, vinyl versatate or vinyl propionate;
- of vinyl halides;
- and their mixture.

4. The process as claimed in the preceding claim, characterized in that the emulsion additionally comprises other ethylenically unsaturated monomers, (co)polymerizable with the monomers of the preceding claim, chosen from the group consisting of:

- unsaturated ethylenic mono- and dicarboxylic

acids, such as acrylic acid, methacrylic acid, itaconic acid, maleic acid or fumaric acid;

- monoalkyl esters of the abovementioned dicarboxylic acids with alkanols, preferably having from 1 to 4 carbon atoms, and their N-substituted derivatives;

- amides of unsaturated carboxylic acids, such as acrylamide, methacrylamide, N-methylolacrylamide, methacrylamide and N-alkylacrylamides;

- ethylenic monomers comprising a sulfonic acid group and its alkali metal or ammonium salts, such as vinylsulfonic acid, vinylbenzenesulfonic acid,  $\alpha$ -acrylamidomethylpropanesulfonic acid or 2-sulfoethylene methacrylate;

- unsaturated ethylenic monomers comprising a secondary, tertiary or quaternary amino group or a heterocyclic group comprising nitrogen, such as, for example, vinylpyridines, vinylimidazole, aminoalkyl (meth)acrylates and

aminoalkyl(meth)acrylamides, such as dimethylaminoethyl acrylate or dimethylaminoethyl methacrylate, di(tert-butyl)aminoethyl acrylate or di(tert-butyl)aminoethyl methacrylate or dimethylaminomethylacrylamide or dimethylaminomethylmethacrylamide;

- zwitterionic monomers, such as sulfopropyl(dimethyl)aminopropyl acrylate;

- and their mixture.

5. The process as claimed in claim 4, characterized in that the direct in-line monitoring is carried out continuously for the preparation of  
5 styrene/butadiene latex by the aqueous emulsion (co)polymerization of styrene with butadiene.

6. The process as claimed in any one of the preceding claims, characterized in that the direct in-line monitoring is carried out for the preparation of a  
10 latex by emulsion (co)polymerization in which the continuous phase is composed of water.

7. The process as claimed in any one of the preceding claims, characterized in that the intensity (area or height) of the specific lines of the Raman  
15 scattering spectrum is calculated:

- on the one hand, at approximately  
1 635  $\pm$  100  $\text{cm}^{-1}$ , a line associated with the stretching vibration of the carbon-carbon double bond of the free monomers which have not yet  
20 (co)polymerized,  
- and, on the other hand, at approximately  
1 660  $\pm$  100  $\text{cm}^{-1}$ , a line associated with the stretching vibrations of the carbon-carbon double bonds incorporated in the main chain of the  
25 polymer obtained when the monomer mixture comprises at least one diene compound.

8. The process as claimed in one of

claims 1 to 6, characterized in that the direct in-line monitoring is carried out by calculating the concentrations of free monomer(s) and of the polymer obtained by multivariable chemometric analytical methods, this calculation being made by a computer having in memory equations establishing a correlation between the Raman spectra and the concentrations of free monomer(s) and of the polymer obtained and the measured Raman spectra being introduced into said memory in order to calculate the concentrations of free monomer(s) and of the polymer obtained during the polymerization.

9. A latex-based composition capable of being obtained by the emulsion (co)polymerization process as claimed in any one of the preceding claims.

10. A device for the direct in-line monitoring *in situ* of the process for the preparation of a latex with predefined properties by emulsion (co)polymerization of ethylenically unsaturated monomers as claimed in any one of claims 1 to 8, comprising:

- (i) a reactor comprising at least one means for feeding with monomers, with surfactants, with (co)polymerization initiator and with water;
- (ii) at least one optical probe which makes it possible to analyze the contents of the reactor;
- (iii) a Raman spectrometer;

(iv) at least one optical fiber

- via which fiber incident light radiation with a wavelength of between 200 nm and 1 400 nm, and preferably between 700 nm and 1 400 nm, is conveyed from the Raman spectrometer to the optical probe,
- and via which fiber the light scattered by the reaction medium is reconveyed to the spectrometer providing the Raman spectrum, the optical fiber being identical or different for the conveying and the reconveying;

(v) a calculator, coupled to the spectrometer, making it possible to calculate, from the Raman spectrum:

- a) either the intensities (areas or heights) of specific lines of the spectrum
  - of un(co)polymerized free monomer(s) in the reaction medium
  - and of the polymer obtained,
- b) or the concentrations of un(co)polymerized free monomer(s) in the reaction medium and of the polymer obtained, from the Raman spectrum using quantitative spectral analytical methods, these methods preferably being multivariable chemometric methods;

(vi) and an adjusting automaton in which is

programed at least one mathematical algorithm making it possible to adjust the reaction parameters, such as the temperature, the pressure, the rate of stirring of the medium and the feeding with monomers, in order to minimize the difference between the process data measured in-line and the reference process data; the process data being based on an algebraic transformation either of the line intensities or of the concentrations of free monomer(s) and of the polymer obtained, and the reference data), based on this same algebraic transformation, being specific data of the process for the production of the latex with predefined properties.

11. The device as claimed in the preceding claim, characterized in that the adjusting automaton is a programable device comprising at least one mathematical algorithm, said device being in contact with the calculator coupled to the Raman spectrometer, makes it possible to act continuously on the parameters of the process to reproduce a predetermined instantaneous conversion profile.

12. The device as claimed in either one of claims 10 and 11, characterized in that the Raman spectrometer is a Fourier transform Raman spectrometer and comprises a light radiation source, an interferometric optical system, a detector, an



electronic system and a computing system.

13. The device as claimed in any one of claims 10 to 12, characterized in that the optical probe is directly positioned close to the reactor in which the (co)polymerization takes place, without distinction

- either in contact with the reaction medium,
- or placed behind a window, so that there is no physical contact between said probe and the reaction medium.

14. The device as claimed in any one of claims 10 to 13, characterized in that the probe comprises one or more means intended to weaken and/or to remove the interfering spectrum or spectra.

15. The device as claimed in the preceding claim, characterized in that the probe comprises a first means intended to remove the Raman spectrum produced by the optical fiber transporting the incident irradiation and a second means intended to weaken the Rayleigh scattering of the probed molecules.

16. The device as claimed in any one of claims 10 to 15, characterized in that the first and second means are optical filters chosen in particular from holographic filters, dielectric filters and dichroic filters.

17. The device as claimed in one of the preceding claims 10 to 16, characterized in that the

transmission of the incident radiation and scattered radiation takes place via optical fibers comprising individual and separate inlet and outlet ports.

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